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MICROSTRUCTURE OF CERAMICS  
FABRICATED BY UNIDIRECTIONAL SOLIDIFICATION

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16. Abstract The unidirectional solidification methods are zone melting, crystal pulling, Bridgemen, and slow cooling. In order to obtain excellent properties (such as transparency), pores, voids and cracks must be avoided, and elimination of such defects is described.					
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# MICROSTRUCTURE OF CERAMICS FABRICATED BY UNIDIRECTIONAL SOLIDIFICATION

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## 1. Introduction

Multi-crystal oxides have been fabricated, most often /176\* so far, by sintering crystal powder or crystallizing glass. Or, to make multi-crystal metal, the melt used to be directly crystallized (solidified). However, this technique has been rarely [1] applied to oxides, except when some particular bricks were made. The reason is that it is difficult to make dense multi-crystal bodies of oxides by the same technique used for metal casting, which consists of the processes of melt draining in a mold and solidifying it by natural cooling. The melt of an oxide is too viscous, the volume shrinks a great deal when it is solidified, and the heat conductivity of its crystals is too low.

However, if an oxide melt is cooled and solidified in only one direction, which is called unidirectional solidification, it will not only form densely packed crystals, but also some particular multi-crystal configurations can be obtained, as shown in Figure 1, when the right conditions are applied. These special multi-crystal configurations include the transparent multi-crystal body consisting

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\*Numbers in the margin indicate pagination in the foreign text.

of columns of one type of crystals standing parallel and containing no pores, or whose crystal columns developed to a specific direction, as shown in Figure 1(a); a complex multi-crystal body, consisting of thin plates of two types of crystals standing alternately parallel next to each other, as shown in Figure 1(b); and a complex multi-crystal body which has a basic crystal phase in which the wire shaped crystal phases are disposed parallel to others, as shown in Figure 1(c). These multi-crystal bodies of

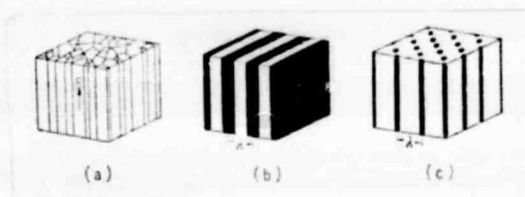


Figure 1. Microstructure of multi-crystal bodies fabricated by unidirectional solidification of melts

such configurations are different from those fabricated by other techniques. They show the electric, magnetic, optical and mechanical properties particular to them. That is why this technique has been applied recently to various kinds of oxides experimentally.

The following discussions concern the method for solidifying the melt unidirectionally and the conditions necessary to obtain the special multi-crystal configurations that were discussed above.

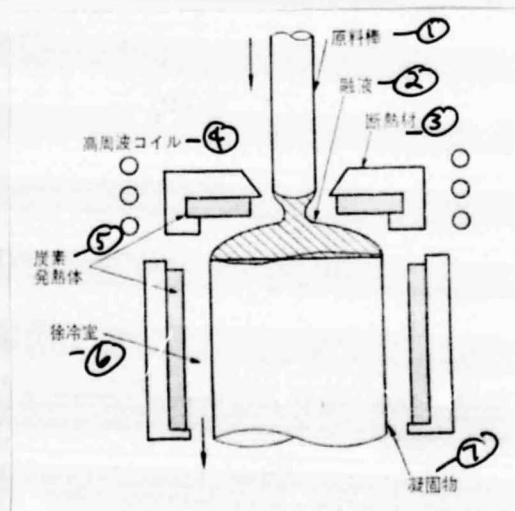
## 2. Unidirectional Solidification

The following discusses the techniques for fabricating multi-crystal bodies by solidifying the melt unidirectionally. All of these techniques are similar to those for fabricating a single crystal from a melt. In the case of multi-crystal bodies, fabrication conditions are not required to be controlled as strictly as a single crystal. And, a single crystal is used as a seed for fabricating single crystal, while multi-crystals are used as seeds for fabricating multi-crystals.

### 2.1 Zone Melting

A raw material stick, made by powder sintering or melt casting, is kept standing vertically in the center of the circular furnace which is kept in the horizontal balance, and the stick is melted from the bottom up as it is lowered at a fixed speed. [2]-[6]

Figure 2 illustrates one of the examples of this type of



#### Keys

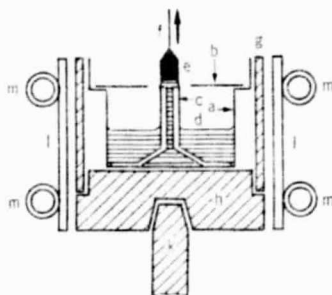
1. Raw material stick
2. Melt
3. Insulator
4. High frequency coil
5. Carbonic pyrogen
6. Slow cooling chamber
7. Solid

Figure 2: An Example of Zone Melting

apparatus. When the solidification speed is smaller than the lowering speed of the stick, the solid horizontal size will be greater than that of the raw material stick. This technique's advantage is that a great temperature gradient can be applied on the crystal-melt boundary surface, but this technique does not work for the fabrication of the solid of shapes other than a stick.

## 2.2 Crystal Pulling

The melt in a container is pulled out from the top at the fixed speed as it solidifies. One of the apparatuses used for this technique is illustrated in Figure 3. In addition to the stick type,



- a. Platinum crucible
- b. Lid
- c. Pattern
- d. Melt
- e. Solid
- f. Platinum wire
- g, h, k. Refractory material
- l. High frequency coil
- m. Water cooling copper pipe

Figure 3: An Example of Crystal Pulling

tubular or plate type solids may be fabricated by placing the proper pattern on the surface of the melt. However, this technique may not be applied to the melt of high vapor pressure.

### 2.3 Bridgman

The raw material powder is put in the cylinder type container, which is placed in a tubular furnace and is lowered at a fixed speed. The powder is melted and solidified from the bottom up. [6][9-13] Figure 4 shows one of the examples of the apparatus used for this technique. This technique may be applied to the melt of high vapor pressure because the container can be tightly closed, but it may not be applied for fabricating other types of solids except sticks.

Keys:

1. Molybdenum wire
2. Molybdenum crucible
3. Graphite pyrogen
4. Zirconium insulator
5. Silica glass tube
6. Induction coil
7. Zirconium support table

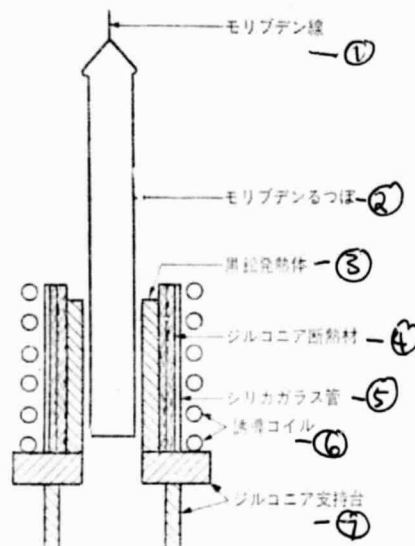


Figure 4: An example of Bridgman technique

### 2.4 Temperature-Gradient and Slow-Cooling Technique

The crucible containing a melt is placed in a furnace that is heated to the different gradient temperatures. The temperatures are lowered at a fixed speed as maintaining the gradient, and the melt is solidified in one direction from the bottom up. [14]-[24] Figure 5 shows one of the apparatus used for this technique. This technique is most appropriate to be applied for the fabrication of large size solids, but the disadvantage is that it is difficult to apply



Keys:

1. Thermocouple
2. Refractory material
3. SiC pyrogen
4. Pt crucible
5. Thermocouple
6. Melt
7. Thermocouple
8. Seed crystal
9. SiC pyrogen

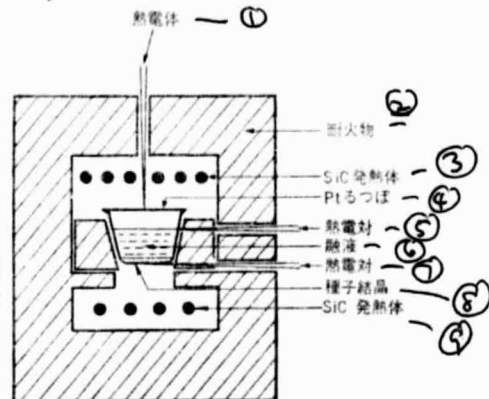


Figure 5: Example of gradient-temperatures and slow-cooling technique

temperatures with the high gradient difference on the crystal-melt field plane.

3. Microstructure of Solid: The Identical Melt Composition

When the melt takes the composition  $C_c$  of Figure 6, which represent the identical or near identical compositions, the melt

Keys:

1. Temperature
2. Composition
3. Liquid phase
4. Liquid + solid phases (A)
5. Liquid + solid phases (B)
6. Solid (A) + solid (B)

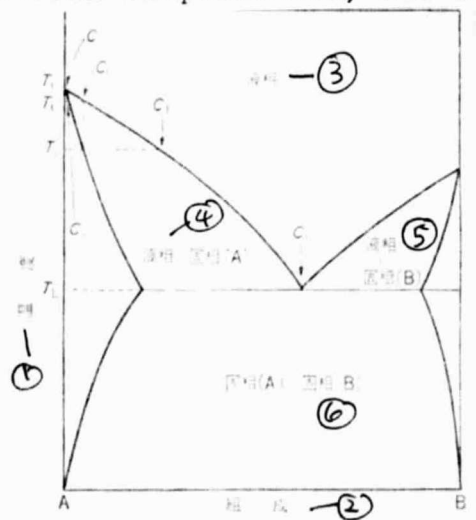


Figure 6: An example of phase equilibrium

solidifies in the configuration shown by Figure 1(a) and produces either a transparent or directional multi-crystal body made of one type of crystals if the right conditions are applied and it is solidified in one direction.

### 3.1 Pores in the Solid

To fabricate a transparent multi-crystal body, pores should not be grown in the solid during the fabrication process. Air bubbles and voids and cracks may be considered as the cause for developing pores.

#### 3.1.1 Air Bubbles

H<sub>2</sub>O and other gases are usually dissolved in the oxide melt, but these gases are hardly dissolvable in crystals. The dissolved gas pours in the melt located in front of crystals as the melt solidification progresses, and the gases eventually diffuse and dissipate gradually from the front of crystals. But, the gas concentration there grows higher rapidly, as the solidification progresses, especially when the solidification speed is high, gas exhaust speed high consequently, and the melt viscosity high, since these reduce the gas diffusion speed. These gases will keep growing, eventually past the tolerable saturation point, and generate air bubbles. [26] These air bubbles will float in the melt, among which the bubbles of small diameter will be trapped by the crystals growing from underneath and will form pores in the solid. Therefore, it is required to choose the particular

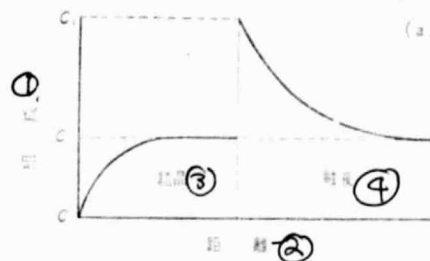
small solidification speed when the high viscosity melt is used for fabricating the type of solid which does not contain pores generated by gases, since air bubbles should not be grown.

### 3.1.2 Void

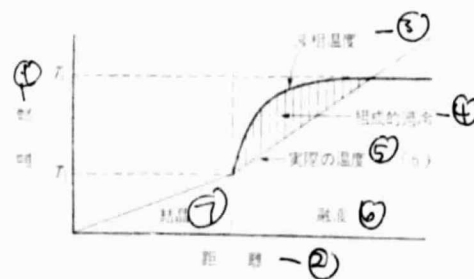
When the solidification speed is great and the temperature gradient is small, the latent heat generated by solidification is stored in the neighborhood of crystal-melt boundary surface. This lowers the temperature of the melt in front of the boundary surface lower than the boundary surface temperature. That area may be

Keys:

1. Composition
2. Distance
3. Crystal
4. Melt



1. Temperature
2. Distance
3. Liquid phase temperature
4. Composition
5. Actual temperature
6. Melt
7. Crystal



1. Crystal
2. Melt
3. Cell structure

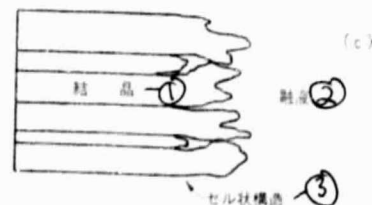


Figure 7: The compositional excessive cooling and cell structure when the melt composition does not match the identical one

cooled excessively. When the melt composition is slightly different from the identical one represented by  $C'_c$  in Figure 6, the composition in the crystal-melt boundary surface area will change to that as indicated by Figure 7(a). This change will also cause the temperature change of the liquid phase in the same area to that represented by Figure 7 (b). In such a case, excessive cooling ( compositional excessive cooling) can easily occur in the melt located in front of the crystal-melt boundary surface, as shown in Figure 7 (b), when the solidification speed is great, temperature gradient small, but when there is no solidification [27] latent heat stored. When this type of excessive cooling occurs, the crystal-melt boundary surface will not take such a flat form, but it will have a rough surface with protrusions and concaves. It is called a cell structure and shown in Figure 7(c). If the size of concaves is great, the melt left in the concaves solidifies slowly, and prevents the melt from being supplied to the area [21][28] where the volume has shrunk; thus, voids are left there. Therefore, in order to avoid fabricating the solid that has pores made by the volume shrinkage, the melt whose composition is as close as possible to the identical one needs to be solidified at a low speed and great gradient temperatures so that the cell structure will not grow enormously.

### 3.1.3. Cracks

During the process cooling the crystals from the solidification temperature to room temperature and when the precipitated crystals shrink by the effect of heat and changes the crystal direction or they switch the phases and change the volume, the solid may not

[19][21][26]-[29]  
contain pores at the beginning but may have them at room temperature.  
The pores are grown by the cracks caused by the thermal stress.  
For preventing the growth of such cracks, the effective measure  
is to add a small amount of components to grow glass in the melt  
and have thin glass phase grow in the precipitated crystals during  
[9][26]-[30]  
the solidification process. This glass phase mitigates the thermal  
stress by its viscous fluidity and suppresses the crack growth while  
the solid is cooled down to room temperature.

If pore, void and crack growth is suppressed, it is  
possible to obtain transparent multi-crystals. The transparent  
multi-crystals that have been obtained by the unidirectional  
solidification include  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ,  $0.7\text{NaNbO}_3 \cdot 0.3\text{BaTiO}_3$   
[14][16] [22]  
[20][24]  
and  $\gamma\text{-Bi}_2\text{O}_3 \cdot \text{SiO}_2$ . Figure 8 shows a photograph of a transparent  
multi-crystal body of  $\gamma\text{-Bi}_2\text{O}_3 \cdot \text{SiO}_2$ . This crystal body shows the  
photo conductivity as superior as a single crystal.

unidirectional  
transparent  $\gamma$

Figure 8: A  $\gamma\text{-Bi}_2\text{O}_3 \cdot \text{SiO}_2$  transparent multi-crystals  
(thickness, 1 mm)

The requirement for fabricating directional multi-crystals by the unidirectional solidification of the melt is that a large number of seed crystals should exist and the crystal precipitation speed of each crystal direction vary with large differences. When a melt is solidified unidirectionally in such conditions, each granule in the seed crystal layer grows to the crystal direction to which the highest granule growth speed is oriented to. When the configuration of each granule is not in an order in the seed crystal layer, the growth direction is not in a regular order in the initial stage, as shown in Figure 9. But, the crystals whose

Keys:

1. Melt
2. Crystals
3. Seed crystals

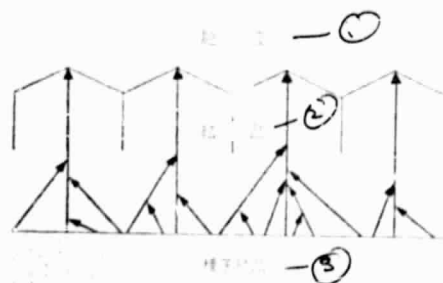


Figure 9: The process where the directional multi-crystals are formed

growth is oriented toward the direction other than the temperature gradient direction (the direction that the melt is fed) eventually slow down their growth as they run into other crystals surrounding them. Thus, only the crystals which are growing to the direction of the temperature gradient will continue to grow, and ultimately the crystals growing toward the temperature gradient direction at the highest speed will remain

[21]

growing and constitute the directional crystal body.

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The directional multi-crystals that have been fabricated by the unidirectional solidification of melt include  $\text{Li}_2\text{O} \cdot$   
 $2\text{SiO}_2$  ( $\langle 001 \rangle$ ) [17],  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{I}_3 \cdot 4\text{SiO}_2$  ( $\langle 110 \rangle$ ) [19],  $\text{Ba}(\text{Zn}, \text{Fe})_2\text{Fe}_{12}\text{O}_{22}$  ( $\langle 110 \rangle$ ) [29],  
 $\text{Bi}_2\text{PbNb}_2\text{O}_9$  ( $\langle 010 \rangle$ ) [21],  $\text{PbTiO}_3$  ( $\langle 110 \rangle$ ) [28] at the solidification speed  
 2 mm/h,  $\langle 001 \rangle$  at 40 mm/h). Figures in parentheses indicate the crystal direction. The direction of  $\text{PbTiO}_3$  varies according to different solidification speeds. These directional multi-crystals are expected to show superior dynamic, thermal and magnetic or electric properties in the solidification direction.

#### 4. Microstructure of the Solid: Eutectic Composition

When the melt takes the composition indicated by  $C_E$  of Figure 6, the eutectic or near eutectic composition, the complex multi-crystals of two different configurations of right orders, shown by (b) or (c) in Figure 1, may be fabricated when it is solidified unidirectionally in the appropriate conditions.

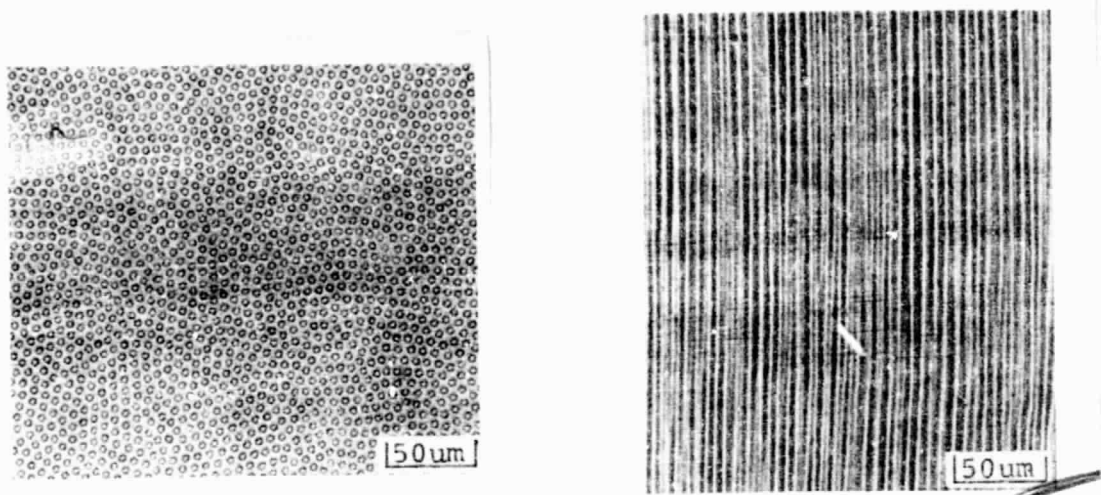
##### 4.1 Configurations of Regular Orders

The requirement for obtaining the solid of the configuration of the regular order discussed above, according to Hunt et al., is that at least one of the two eutectic crystal phases should have the melting entropy ( $\Delta S_f$ ) smaller than  $2R$  ( $R$ , a gas constant), because the crystals with  $\Delta S_f$  larger than

2R are likely to take their own particular facet form.

However, the question whether the crystal takes in reality the facet form or not does not only depend on  $\Delta S_f$ , but the melt composition, temperature gradient, solidification speed are also affecting factors. Therefore, it seems that the most significant requirement for fabricating the solid of regular configuration is that both the eutectic crystal phases should grow in the form of flat crystal-melt boundary surface instead of cell structure. The effective technique for growing eutectic crystals with the flat crystal-melt boundary surface, instead of in the cell structure, is to prepare the melt of the eutectic composition as close to perfect as possible and to solidify it in the great temperature gradient at a low speed, so that an excessive cooling will not occur in front of the crystal-melt boundary surface, just as it was needed to be avoided with the identical melt composition. But, when the liquid phase temperature does not vary as different compositions are used, an excessive cooling does not occur in front of the crystal-melt boundary plane even if the melt composition is not very close to the perfect eutectic composition; therefore, a solid of regular configuration may be obtained. In such a case, the volume ratio of the two types of crystals may be varied in a large range. Figure 10 illustrates some examples of the solids with such regular configurations. Because the wire structure crystals in this solid has the refraction rate higher than that of the surrounding matrix, this multi-crystal body shows the function same as that of the clad type photo-fiber bundled in the high density. These crystals have the color similar to that of cat's eye stone.





(a) Cross section vertical to  
the solidification direction

(b) Cross section parallel to  
the solidification direction

Figure 10: The microstructure of the eutectic composition solids  
of  $\text{Bi}_2\text{O}_3(\text{Nb}_2\text{O}_5)\text{-}6\text{Bi}_2\text{O}_3\text{ SiO}_2$  type.

Wire type crystals:  $\delta\text{-Bi}_2\text{O}_3(\text{Nb}_2\text{O}_5)$ ;

Matrix:  $\gamma\text{-}6\text{Bi}_2\text{O}_3\text{SiO}_2$

#### 4.2 Either Thin Plate or Wire Structure

The question whether the regular order solid takes the thin plate structure, as shown by (b) of Figure 1, or the structure as wire, as illustrated by (c), depends on the question which structure has the smaller energy on the boundary surfaces among crystals. The boundary surfaces area among crystals of the thin plate structure remains the same per unit volume of complex crystals, in the case of the thin plate structure, as shown in Figure 11. In the case of the wire structure, the

Keys:

1. Volume rate of the phase smaller than the other
2. Boundary surface area/ volume rate
3. Thin plate structure
4. Wire structure

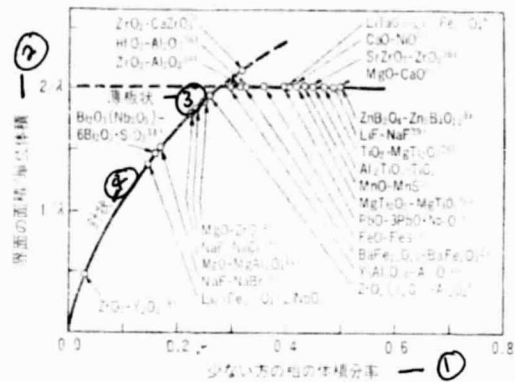


Figure 11: The relation between vlume rates of composing crystal phase and crystal boundary surface area.

[36]

(The diagram is supplied by Minford et al.

[34]

Additional data supplied by us.)

boundary surface area increases as the volume rate of the wire structure crystals increases, as shown in Figure 11. When the volume rate of the wire structure crystals is 0.28, its surface area equals to that of the thin plate structure crystals. In consequence, complex multi-crystals take the wire structure when the volume rate of the smaller phase of the two is less than 0.28, and they take the thin plate structure when it is greater than 0.28. In Figure 11, marking of the solids that have been reported to have taken the wire structure is made on the line representing the boundary surface of the wire structure; and of the solids which have been reported to have taken the thin plate structure, on the line representing the boundary area of the thin

plate structure, and both structures are marked at the point representing the volume rate of the smaller phase. The diagram indicates that the crystals actually take on a wire structure when the smaller phase's volume rate is smaller than 0.28, and thin plate structure when it is greater than 0.28. The  $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-Al}_2\text{O}_3$  type solid indicated in Figure 11 takes the structure where  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  array parallel in a high density in the matrix  $\text{Al}_2\text{O}_3$ , and this multi-crystal body shows a great mechanical strength at room temperature or temperatures as high as  $1500^\circ\text{C}$ , much greater than that of alumina multi-crystals made by hot press process.

### 4.3 Distance Between Crystals

The distance  $\lambda$  between the centers of crystals of the same structure, either thin plate or wire type, is determined by the balance between two forces: one that tries to keep  $\lambda$  small so that the horizontal diffusion distance of the crystal components is kept

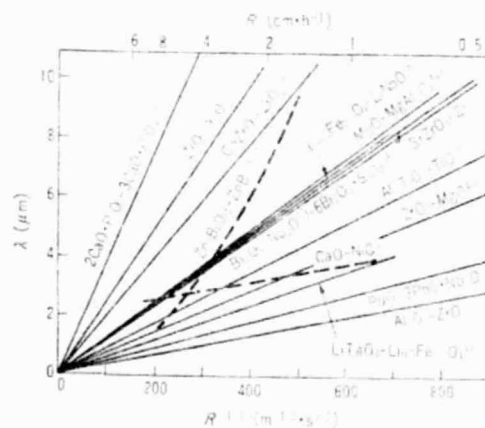


Figure 12: The relation between crystal distance and solidification speed R [36]  
(The diagram is supplied by Minford et al., and more data added by us. [23][34])

short, and the other force that tries to keep  $\lambda$  great so that the boundary surface area between the two types of crystals is kept [37] small. Consequently,  $\lambda = CR^{1/2}$  (C is a constant determined by the melt composition) is set as the relation between  $\lambda$  and the solidification speed R. Figure 12 shows the relation between  $\lambda$  and R of some solids of thin plate and wire structures that have [23][34][36] been reported. It is clear, from this figure, that the above mentioned relation is observed in many systems.

## 5. Postscript

The above discussion outlines multi-crystals of what characteristic microstructure can be obtained and what are the requirements for fabricating the multi-crystals of such characteristics microstructure. We tried to avoid using formulae as much as possible in this paper. If any reader wishes to find more details of such information, we hope that he will use the reference materials listed in each chapter and other materials listed in the bibliography, No. 41-44. The multi-crystals fabricated by [9,20,24,45,47,48] unidirectional solidification show particular electric, [6,29,45,47,48] [6,18,20,24,25-27,51] [19] [3,6,40,49,50] magnetic, optical, thermal, and dynamic nature, but we were not able to discuss them much in this report. Please use the reference and bibliography on these points also. Additionally, one of the techniques developed from the melt unidirectional solidification is the method, which is to freeze hydrogel unidirectionally in place of melt, then to melt the ice portion at room temperature, and to fabricate porous non-crystal fiber. This was done recently as an experiment.

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